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Validation of the Semi-Volatile Organic Sampling Train Method for Measuring Emissions from Hazardous Waste Incinerators

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VALIDATION OF THE SEMI-VOLATILE ORGANIC SAMPLING TRAIN METHOD FOR MEASURING EMISSIONS FROM HAZARDOUS WASTE INCINERATORS

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16. ABSTRACT

A formulation of the methodology for determining semi-volatile organic emissions from hazardous waste incinerators was subjected to an intensive series of laboratory experiments to determine the viability of the method. Using a selected series of test compounds, a method detection limit was established for GC/MS quantitations of each species. A matrixed-experiment was performed to evaluate the recovery of the test compounds introduced into a flue gas simulation system under two levels of component concentration and mixed with moisture, HCl, SO_2, and NO_x. Low recoveries were measured for pyridine and urethane and will require further study. The methodology was insensitive to the environment variables introduced by the flue gas simulation experiments.

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Introduction

In the United States, the disposal of hazardous waste is regulated by the Resource Conservation and Recovery Act (RCRA). Included in the regulations are provisions for waste disposal by incineration. To provide for environmental protection during the operation of such hazardous waste incinerators, RCRA requires that a destruction and removal efficiency (DRE) of equal to or greater than 99.99% be met for certain pre-determined principal organic hazardous constituents (POHCs) of the wastes being incinerated. The determination of a DRE for a particular POHC requires the use of standardized sampling and analysis methods.

In general, POHCs are defined as a listing of chemical compounds which is presented in Appendix VIII within RCRA (40 C.F.R., Part 261). The U.S. Environmental Protection Agency has published a compendium of sampling and analytical methods to be used in determining the concentrations of POHCs in discharges from incinerators[1]. Methods are presented for application to various segments of the incineration process, including the waste feed, aqueous effluents (cooling water or spent scrubber liquor), fly or bottom ashes, and stack gas. The methodology employed for the measurement of POHCs from stack gases varies according to the range of boiling points of the specific Appendix VIII compounds anticipated to be present in the sample stream. Compounds with boiling points less than 100°C are termed volatile POHCs while those boiling at temperatures greater than 100°C are semi-volatile POHCs. The work presented in this paper focuses on the validation of a sampling and analytical method for the determination of semi-volatile POHCs in stack gases emitted from hazardous waste incinerators. Various similar versions of the methodology have been identified in waste incinerator operating permit applications over the past four years, and are commonly referred to as either the Semi-Volatile Organic Sampling Train (Semi-VOST) or the Modified Method 5 Train (MM5)[2]. A version of the MM5 methodology has recently been proposed as a standard method for hazardous waste incinerators[3].

The major focus of this validation study of the Semi-VOST method was directed to determine precision and accuracy of the method which are applicable under actual operating conditions. However, prior to the field evaluation of the method, a number of laboratory studies were performed to evaluate the sampling train configuration and the analytical protocols. The validation scheme was comprised of a number of sequential tasks, including:

1. evaluation of the method formulation,
2. construction of the Semi-VOST sampling hardware,
3. selection of test compounds to challenge the sampling and analytical protocols,
4. Semi-VOST laboratory evaluation study, and
5. Semi-VOST field evaluation study.

This paper presents a discussion of Tasks 1-4 of the validation study. At this time, a field sampling experiment has been performed to address Task 5 but laboratory analyses of the samples have not been completed and evaluated. The results of that work will be reported at a later date.

Method Formulation

The method formulation employed in this study is cited in Reference 1. That formulation contains several sections that are discretionary or that require clarification. Therefore, prior to laboratory experimentation, a refinement in the formulation was developed by surveying members of the technical community that had experience in the use of the Semi-VOST method. Thus, a working copy of the method was proposed that clarified certain sections and that added missing elements to the procedure. Emphasis was given to detailing an analysis scheme which was often found missing in many Semi-VOST method write-ups.

In the application of Semi-VOST, gaseous and particulate components are isokinetically withdrawn from an emission source and collected in a multicomponent sampling train. Two key elements in the train include a high-efficiency particulate filter and a packed bed of porous polymeric adsorbent resin. The filter is used to separate stack gas particles from gaseous substances which are adsorbed on the resin. Following sample collection, the resin is extracted with solvent and the extracted components are concentrated and are identified/quantified using high resolution gas chromatography coupled with low resolution mass spectrometry. Porous polymers have been widely used for the collection and concentration of organic materials in air and water environments. As a collection sorbent, XAD-2, a polystyrene-divinylbenzene copolymer, has the advantage of high surface area (300 m^2/g) with a relatively small average pore volume (90 Å) which affords both the capacity and selectivity for collection of semi-volatile compounds.

Figure 1 presents a schematic of the Semi-VOST sampling train. The configuration is an adaptation from EPA Method 5[4] and contains several elements of that train. Additional components include a condenser coil with a sorbent module used to collect the POHCs from the stack gases. Details of construction for the basic elements of the train are discussed as part of the Method 5 description. Details of the train are discussed here for clarification.

The organic sampling module, illustrated in Figure 2, consists of three elements; a gas cooling condenser, sorbent trap, and a condensate collector. The gas cooler should be capable of maintaining the temperature of the sample stream leaving the back half of the filter holder below 20°C to insure the collection of organic compounds with low elution volumes. The sorbent trap is sized to contain approximately 40 grams of XAD-2. Cooling water is furnished by a peristaltic pump drawing from the impinger ice water bath. The sorbent trap is outfitted with a thermocouple well for monitoring the sample gas entry temperature. The sorbent module must be oriented to direct the flow of condensate vertically-downward from the cooling condensor, through the resin bed, and into the condensate knockout trap. The vertical

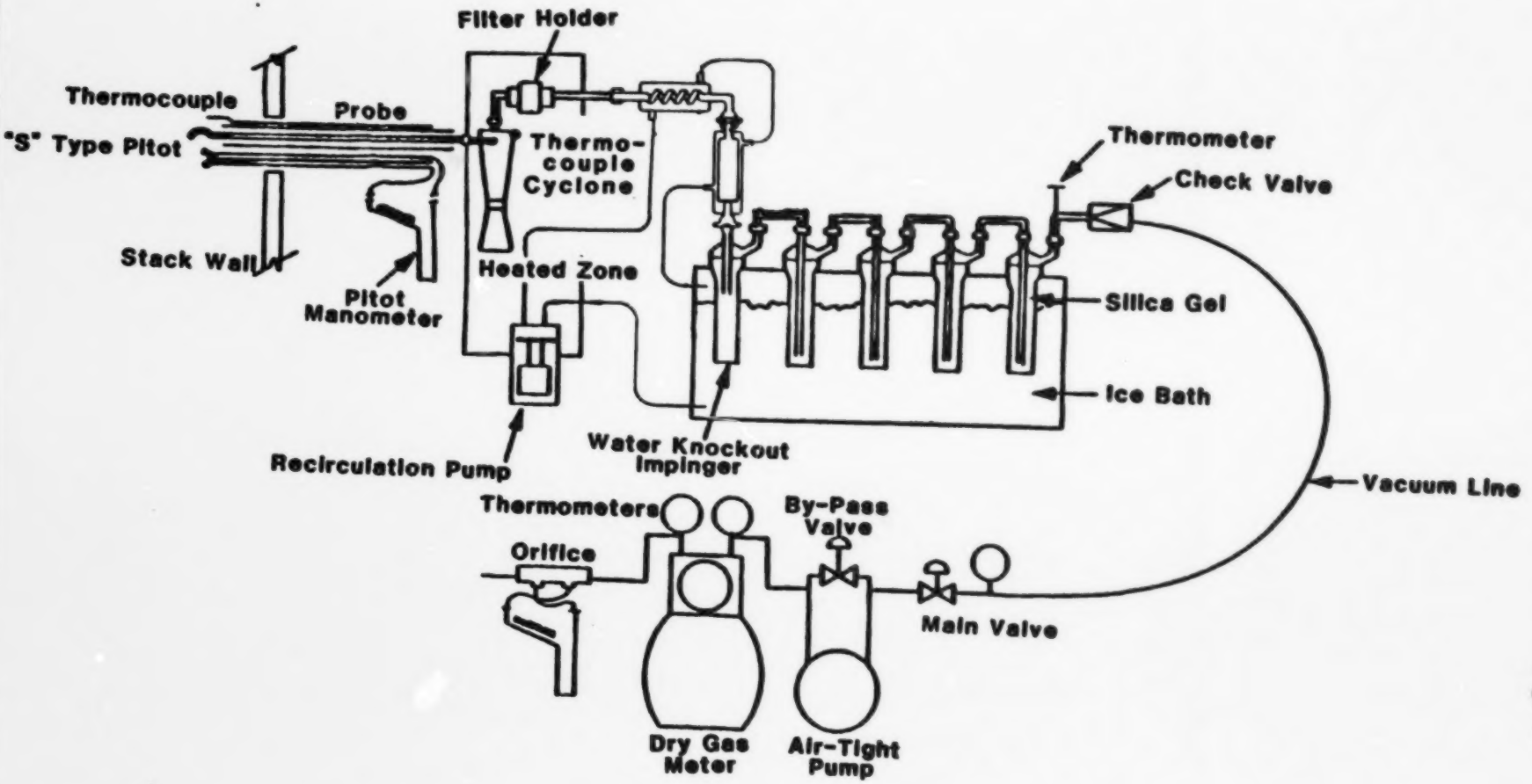
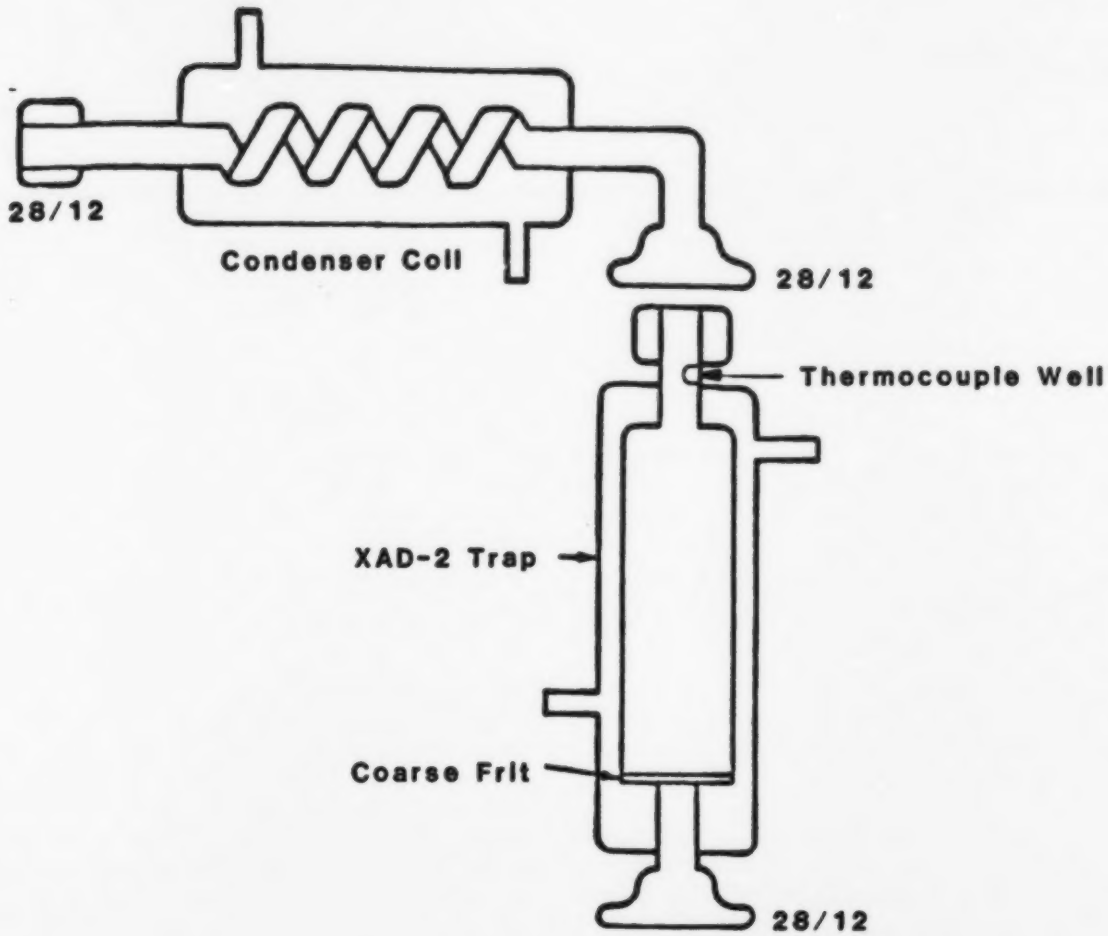


Figure 1. Semi-VOST train schematic diagram.



XAD-2 Trap and Condenser Coil

Figure 2. Gas condenser and sorbent module design.

configuration of the XAD-2 module is necessary to avoid channeling of the sample gas and water condensate. In practice, the resin is used to collect POHCs from both media. The knockout trap is used to collect a large volume of condensate without overflowing into the impinger train. This is necessary because sample streams collected from scrubber-equipped incinerators may contain moisture levels exceeding 25 percent by volume. All surfaces from the probe nozzle through the sorbent module must be constructed of inert materials.

The final elements of the train include a series of impingers to collect HCl and water vapor as protective measures for the sample pump and dry gas volume measurement.

Typically, 3 dscm of sample volume is required for the determination of DRE of POHCs from incineration systems. Sampling flow rates are maintained at approximately 0.014 dscm/min. After sampling, the filter pad is removed and retained as a separate sample fraction. The nozzle, probe, cyclone and filter holder are rinsed with methylene chloride and methanol. The rinses are then combined and retained. The condenser, transfer line, and condensate knockout trap are rinsed with the solvent mixture and combined. The sorbent module is plugged and then wrapped in aluminum foil. The first impinger contents are recovered separately from the materials in the second and third impingers which are rinsed and combined. The silica gel impinger is weighed.

Following return of the samples to the laboratory, all fractions are spiked with surrogate standards prior to extraction, concentration, and analysis. The use of surrogates provides a measure of the integrity of the sample preparation procedures. In the sample analyses, an examination of surrogate recovery can be used to qualify the analytical results. For example, poor or variable surrogate recovery could parallel similar variations in POHCs determined in the samples. This behavior would suggest problems with sample preparation/analysis as opposed to incinerator operation. The spiking compounds should be the stable isotopically-labeled analog of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographically separated, and not interfere with the analysis. Potential surrogate spiking compounds include: deuterated naphthalene, chrysene, phenol, 3,4,3'4'-tetrachlorobiphenyl, carbon 13-labeled pentachlorophenol, and 1,2,4,5-tetrachlorobenzene.

The condensate knockout trap solution is spiked with the surrogates, transferred to a separatory funnel, and acidified and then extracted with methylene chloride. The aqueous phase is then made alkaline and re-extracted with methylene chloride. This procedure is used to optimize the recovery of POHCs with varying functional groups. The condensate may contain compounds which show great water solubility and low organic solvent solubility. Alternatively, pH adjustment with solvent extraction is an ion-exchange technique designed to recover such polar compounds. The methylene chloride solutions are combined in a Kuderna-Danish evaporator/concentrator and reduced in volume to usually less than 10 ml and an internal standard is added for quantitation by gas chromatography coupled with mass spectrometry (GC/MS).

The impinger contents are also extracted with methylene chloride under both acidic and basic conditions and then concentrated. Rinses from the probe and filter housing are processed similarly. The sorbent module is spiked with surrogate standards and the resin and particulate filter are transferred to an all-glass Soxhlet extraction thimble. The module container is rinsed with methylene chloride, which is added to the Soxhlet, and extraction is conducted for 16 hours.

Analysis is performed by GC/MS using fused-silica capillary GC columns. The mass spectrometer is operated in a full mass range (40 to 450) scanning mode. For most purposes, electron impact (EI) spectra is collected since a majority of the potential POHCs give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other reference data which aid in identification.

The gas chromatograph should be equipped with fused-silica capillary columns for separation of complex samples. Additionally, the inertness of such columns greatly improves versatility for analysis of both polar and non-polar compounds. The operating conditions for the GC include the following parameters:

- Column: 30 M x 0.25 mm ID fused-silica capillary, coated with SE-54 or equivalent.
- Injector Temperature: 280°C.
- Column Temperature: 25°C for 4 minutes; then raised to 270°C @ 10°C/min. Hold at 270°C until no evidence of eluting peaks.
- Carrier Gas: High-purity helium flowing @ 3 ml/min.
- Injection Volume: 1 ul.

To ensure consistency among sources of mass spectral data, the GC/MS should be tuned to meet the spectral criteria for decafluorotriphenylphosphine as outlined in EPA Method 625[5]. The identification of organic POHCs is based on the chromatographic elution of those compounds and on the specificity of the detection system. The relative retention time of a POHC compared to an appropriate internal standard is generally constant to within about 0.2%, depending on the compound. For analysis by GC/MS, a match in both the relative retention time for the POHCs and the simultaneous elution of multiple analytical ions specific to that POHC will serve to establish the qualitative identification of the components of the sample.

For directed analyses where specific POHCs are to be measured in the sample, the identification criteria to confirm the presence of a POHC by MS are that the GC retention time for the suspect peak relative to some standard match that for the corresponding POHC. Also, the characteristic ions of the suspected POHC must be present in the unknown sample at approximately the same ratio as is present in the standard.

For quantitation by GC/MS, each sample fraction is spiked with a known amount of the internal standard prior to analysis. The response ratio of the internal standard to the compounds of interest in the sample is then compared to a similar ratio established with a calibration curve.

The response factor calibration for the individual compounds is established by using a five-point calibration curve with nominal compound levels of 10, 25, 100, 250, and 500 ug/ml. This calibration is established using the compounds of interest at concentrations that will bracket the working range of the sample concentrations. Sample concentrations can be modified either up or down to fit this range. The samples are spiked with the internal standard so the resulting concentration will fall within the calibration curve.

Additional details of the method formulation will be reported at a later date in a final report.[6] However, the basic elements of the Semi-VOST method have been summarized here to clarify the discussion of the laboratory studies which now follows.

Selection of Test Compounds

Upon formulation of a working draft of the method and procurement/construction of the Semi-VOST sampling gear, the first laboratory studies involved the selection of test compounds (POHCs). The criteria for compound selection included: (1) incinerability; (2) solubility in water; (3) boiling point; and (4) chemical functionality.

Highly-halogenated waste feed components are materials which are difficult to incinerate because of limited C-H bonding. Their presence in the incinerator feed make-up must be carefully controlled along with the incinerator temperature to ensure a high DRE. Alternately, in an improperly-operated incinerator, chlorinated POHCs would be present at relatively high concentrations in the stack gases.

Since XAD-2 was selected as the sorbent resin for the Semi-VOST method because of its ability to adsorb trace organics from both gas phase and aqueous media, a number of water-soluble test compounds were selected to determine the recovery of POHCs from aqueous-scrubbed flue gases. This sampling environment would produce a large volume of condensate passing through the sorbent module.

Additional compounds were selected for study which had a range of boiling points within the applicable limits of the method (100°C). Consideration was also given to challenging the sample extraction elements of the method with both polar and polyfunctional test compounds.

A series of twelve compounds were selected for study which included a range of boiling points from 100°C (toluene) to 310°C (pentachlorophenol). Initial experiments were conducted to determine the method detection limit (MDL) for each of the twelve compounds

combined in a solution of methanol. The analyses were performed using GC/MS with the statistical method of Glaser, et al.,[7] for measuring concentration at successive iterations of component concentrations approaching the MDL. The MDL calculations for each of the test compounds are presented in Table I.

Given the complexity of the sampling and analytical procedures detailed in the Semi-VOST method formulation, it is advantageous to obtain as much performance information as possible before attempting field studies to determine precision and accuracy. Properly-designed laboratory experiments which simulate field sample stream environments can provide data to determine that the execution of the method is in control or to uncover undesirable, determinant characteristics which could be remedied by modifying the procedures prior to use in the field.

Laboratory Experiments

Laboratory experiments were designed to simulate the flue gas environment. Parameters considered to affect method performance included: flue gas water vapor, POHC concentration sample volume and flowrate, HCl, SO_2, and NO_x. Determining method performance for sampling streams containing SO_2 and NO_x is of interest to study the potential for sulfonation and/or nitration of XAD-2. This possibility could either alter the absorptive capacity of the resin for POHCs or create POHC-like artifacts by fragmenting the resin's cross-linked chemical structure.

A flue gas simulator was designed and constructed to evaluate the performance of the method in the laboratory. The simulator, illustrated in Figure 3, was sized to deliver sufficient "stack" gas volume flows to be sampled simultaneously by two Semi-VOST trains through a heated glass manifiold. A hydrocarbon-free air sample stream of 0.56 dscm/min was provided by pumping ambient air through a high temperature catalytic oxidizer and a Perma-Pure® polymeric drier. The air stream was then split with half of the total flow heated to approximately 250°C before introduction of POHCs. Solutions of the test compounds were prepared in methanol and introduced into the hot air stream through a 5 mL motor-driven syringe. Typical solution delivery rates ranged between 20-30 uL/min. The air containing POHCs was then re-heated through a glass mixing bulb before introduction of water, HCl, SO_2, NO and the other half of the clean air stream. Sulfur dioxide and NO were introduced from cylinder gas mixtures. HCl was introduced by acifidying the water being metered into the air mixture. The "stack" gas then passed through a second, heated, mixing bulb before entering a glass sampling manifold heated to about 300°C. The design parameters provided for 20% maximum flue gas moisture levels.

Table II presents a listing of sample generation variables addressed in the study. Table III outlines the test matrix conditions which were based upon a one-half replicate of a 2^5 factorial experimental design. The operating conditions are listed in terms of (1), ab, cd, ae, abcd, etc., as given in the design. The symbol "(1)"

Table 1. Method detection limit (MDL) for GC/MS analysis of test compounds in methanol

Selection Criteria	Test Compound	Boiling Point, °C	MDL ng/uL
Incinerability	1,1,2,2-tetrachloroethane	146	0.25
	pentachlorophenol	310	4.27
	hexachloroethane	(sublimes)	0.90
Water Solubility	urethane	180	10.13
	pyridine	115	8.51
	1,4-dioxane	102	6.98
Boiling Point	naphthalene	218	0.32
	chlorobenzene	132	0.37
	toluene	110	1.85
Chemical Functionality	phenol	182	4.95
	nitrobenzene	211	1.09
	resorcinol	280	7.30

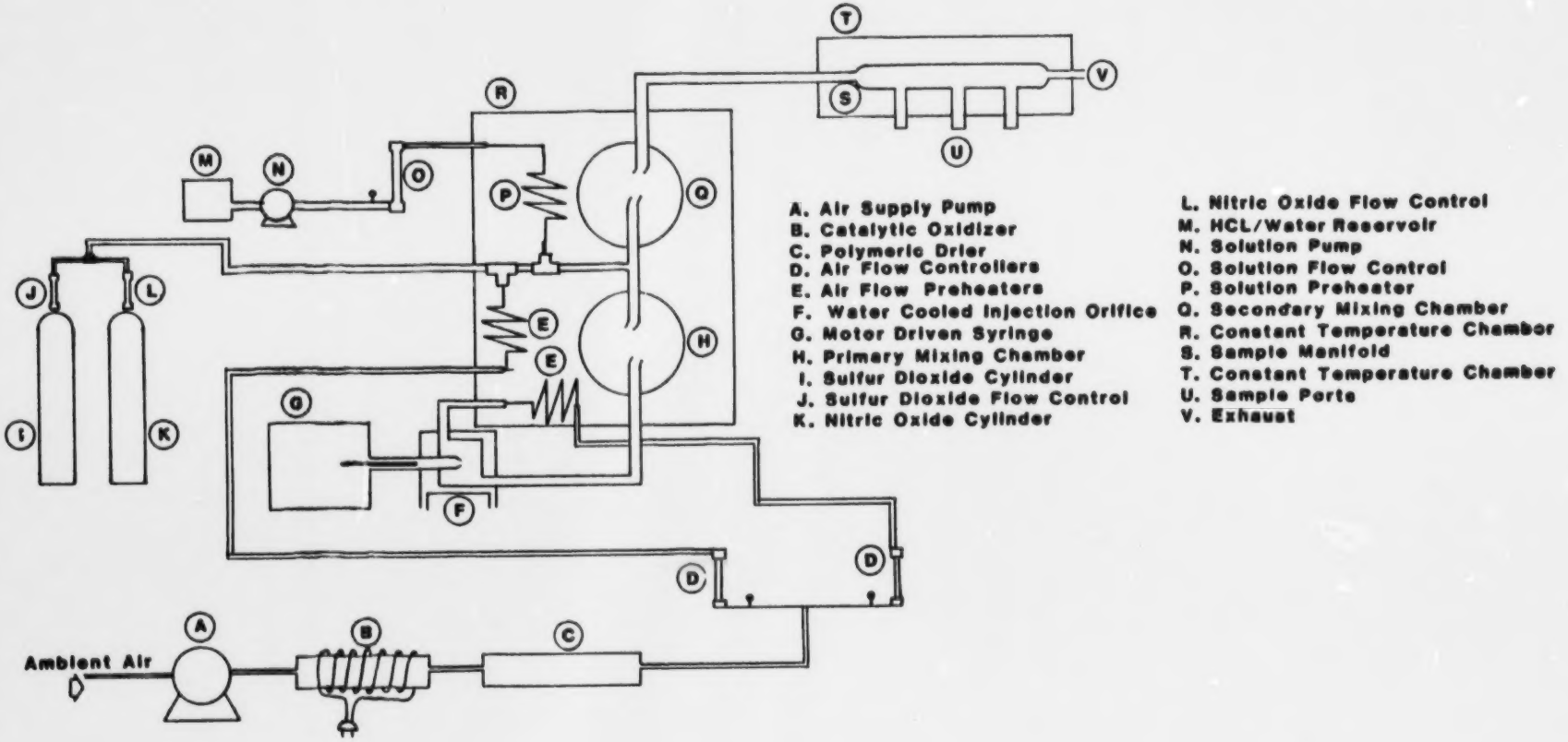


Figure 3. Flue gas simulation system.

Table II. Sample generation variables.

Variable	Level I	Level II
A	Low moisture High SO_2 (~750 ppmv) High HCl (~1,000 ppmv)	High moisture Low SO_2 (~50 ppmv) Low HCl (~50 ppmv)
B	Low NO_x (~250 ppmv)	High NO_x (~1,000 ppmv)
C	Low hydrocarbon concentration (~3 MDL)	High hydrocarbon concentration (~10 MDL)
D	Small sample size (~0.6 m^3)	Large sample size (~14 m^3)
E	Low sample flow rate (~0.0028 dscm/min.)	High sample flow rate (~0.021 dscm/min.)

Table III. 1/2 replicate of a 2^5 factorial experiment.

CD = ABE Confounded With Blocks

Block 1	Block 2
(1)	ac
ab	bc
cd	ad
ae	bd
be	ce
abcd	de
acde	abce
bcde	abde

represents Level I of all five independent operating variables. Symbol "ab" represented Level II of Variable A and Variable B, and Level I for Variables C, D, and E. GC/MS with fused-silica capillary columns was used as the measurement method for all analyses according to the draft method formulation.

A summary of the results for the flue gas generator studies is given in Table IV in which the data are expressed as percent recovery. Runs 1 and 2 were initial experiments in which the test compounds were added at the 10 MDL level to a clean air stream without the addition of SO_2, NO_x, HCl or moisture. The gas stream was sampled by two Semi-VOST trains "A" and "B". These tests were used to provide an indication of the baseline error for the analysis of results. The remainder of the tests were carried out by collecting samples with a single train over the range of test conditions. The range of the recoveries as well as mean recoveries and standard deviations for each compound are given in the table.

The paired replicates of Runs 1 and 2 were evaluated by determining the mean and standard deviation of each compound recovery compared with the corresponding recoveries reported for operating condition "(1)". The results given in Table V show that nine of the twelve test compounds yield recoveries in excess of 80% for Runs 1 and 2. The range of standard deviations for compound recovery varies from 4.1% for naphthalene (93% average recovery) to 16.4% for dioxane (91% average recovery). No recoveries were measured for either resorcinol or pentachlorophenol which may be due to compound pyrolysis and loss within the flue gas simulation system. Of the remaining test compounds pyridine and urethane exhibited either poor or variable recoveries under baseline conditions. The water solubility of these two compounds should not be a mitigating factor since four of the five measurements were taken with no moisture present in the generation system. A recent study[8] reported poor recovery of nitrogen-containing heterocyclic compounds from groundwater extracted with methylene chloride/acetonitrile solvent mixtures. Certain amines will react with methylene chloride in the presence of sodium hydroxide. Therefore, it is possible that pyridine may react during the sample extraction and recovery process. Future experiments are planned to address this area of concern.

For Runs 1 and 2, deuterated surrogates for six test compounds were added in the 10-100 MDL range to the XAD-2 module prior to resin extraction. Their mean recoveries given in Table V are somewhat higher for four of the six comparable test compounds. Both the dioxane and pyridine surrogate recoveries are highly variable. The data for the baseline generator operating conditions compare favorably with the analytical results from operating condition "(1)" during which the generator was injected with POHCs at 3 MDL and operated at low NO/moisture and high levels of SO_2 and HCl. These test conditions simulate an unscrubbed incinerator emission stream.

Examination of the results of measurements conducted under the variety of operating conditions confirms the flue gas simulation problems with pentachlorophenol and resorcinol. The excessive recovery of pentachlorophenol for several tests suggests that the compound was

Table IV. Generator study, summary percentage recoveries.

	Run 1		Run 2		Operating conditions																		
	A	B	A	B	(1)	ab	cd	ae	be	abcd	acde	bcde	ac	bc	ad	bd	ce	de	abce	abde	Range	Mean	Std. dev.
Dioxane	105	83	71	103	100	78	104	112	87	89	133	87	115	67	111	105	114	109	115	101	71-133	99.5	16.7
Pyridine	51	41	31	63	10	41	73	61	14	56	105	88	103	9	69	52	156	27	35	91	9-156	58.8	36.8
Toluene	80	68	82	95	84	84	72	86	75	74	161	93	68	73	117	119	71	141	75	112	68-161	91.5	25.7
Urethane	65	61	74	121*	81	40	48	60	15	32	65	67	67	4	58	38	99	26	59	33	4-121	55.6	27.7
Chlorobenzene	87	71	79	101	90	94	98	107	82	97	123	101	88	85	109	113	93	93	95	110	71-123	95.8	12.55
1,1,2,2-Tetrachloroethane	95	71	84	94	98	105	109	109	86	100	141	113	98	87	99	117	105	104	99	121	71-121	101.8	15.0
Phenol	79	99	77	93	100	71	81	108	66	66	113	105	92	77	81	77	111	86	94	64	64-113	87.0	15.5
Nitrobenzene	85	79	82	101	100	110	107	119	97	106	116	116	108	98	110	131	112	119	110	121	79-131	106.4	13.4
Hexachloroethane	84	80	83	91	100	99	99	117	93	104	104	115	98	101	92	107	101	112	112	102	80-117	99.6	10.3
Naphthalene	92	91	90	99	110	95	100	112	102	100	119	119	95	110	91	110	97	135	101	111	90-135	104.0	11.7
Resorcinol	0	0	0	0	0	0	0	0	23	0	0	1	11	0	0	0	10	0	0	0	0-23	2.3	5.8
Pentachlorophenol	0	0	0	0	0	83	226	169	77	177	-	201	136	22.5	121	120	182	633	219	0	0-633	118.3	167.6

*Suspected outlier.

Table V. Comparison of mean sample and surrogate recoveries for baseline generator and operating condition (1)

	Generator Experiment				Operating Condition (1)
	Runs 1 and 2				
	Sample Train Recovery		Deuterated Surrogate Recovery		
Test Compound	Mean	Std. Dev.	Mean	Std. Dev.	Recovery
1,1,2,2-tetra-chloroethane	86%	11.2%	--	--	98
pentachlorophenol	0	--	--	--	0
hexachloroethane	85	4.7	--	--	100
urethane	67*	5.4	--	--	81
pyridine	47	13.7	72	20.2	10
dioxane	91	16.4	85	22.7	100
naphthalene	93	4.1	--	--	110
chlorobenzene	83	12.8	97	6.9	90
toluene	81	11.1	122	16.5	84
phenol	87	10.7	108	12.4	100
nitrobenzene	87	9.8	102	8.0	100
resorcinol	0	--	--	--	0

*Does not include Run 2, Train B.

accumulating in the generation system and was released intermittently over the course of the study. Also, overall mean recoveries were poor for both pyridine and urethane. Operating condition "CD" should represent the most ideal set of simulation parameters which would be reflected by good test compound recoveries. Condition "CD" corresponds to high test compound levels with a large volume sample collected at low sample flowrate and low levels of moisture. With the exception of urethane, pentachlorophenol, and resorcinol, test compound recoveries ranged from 72-109%.

Operating condition "ab" can be considered the most challenging set of simulation parameters for the method evaluation since a sample was collected under the conditions of high moisture and NO levels with low test compound, sample volume and flowrate levels. With the exception of urethane, pentachlorophenol, resorcinol, and pyridine, test compound recoveries ranged from 71-110%.

An analysis of variance for compound recoveries was performed between and within the experimental block using the data given in Table IV. No statistically significant interaction could be identified between a sample generation variable and compound recovery. Additional aggregations and comparisons of the generator test results included an evaluation of the compound detection limits of the method. Mean recoveries were calculated for ten compounds (pentachlorophenol and resorcinol excluded) sampled under the low concentration (3 MDL) generator conditions. A linear relation between mean recovery and the method detection limit gave a correlation coefficient of -0.87. A similar aggregation and correlation for the same compounds sampled under high concentration (10 MDL) generator conditions gave a correlation coefficient of -0.78. The mean recoveries are higher under high test compound generator levels than for low levels but the standard deviations are also somewhat greater. The latter observation might be due to fluctuations in the generator stability as opposed to variability in compound recovery.

Low compound recoveries could also be explained by artifact formation. An analysis of fifteen different sets of GC/MS data representative of XAD-2 extracts indicated no other compounds present except the test compounds, deuterated surrogates, and solvent contaminants such as phthalates. Therefore, artifact formation is not a problem with the method sampling under the generator test conditions.

Conclusions

A formulation of the methodology for determining semi-volatile organic emissions from hazardous waste incinerators was subjected to an intensive series of laboratory experiments to determine the viability of the method. Using a selected series of test compounds, a method detection limit was established for GC/MS quantitation of each species. A matrixed-experiment was performed to evaluate the recovery of the test compounds introduced into a flue gas simulation system under two levels of component concentration and mixed with moisture, HCl, SO_2, and NO_x.

Mean recoveries were in excess of 90% for a number of the compounds. Low recoveries were measured for pyridine and urethane and will require further study. The methodology was insensitive to the environment variables introduced by the flue gas simulation experiments.

Future Research

A field validation study has been planned to study the precision and accuracy of the method at a hazardous waste incineration facility. This project will involve the simultaneous operation of four sampling trains in a test matrix designed to study spiked-POHC recovery under selected sampling conditions. Also, additional laboratory experiments are planned to address the determination of the variabilities between each of the procedural steps in the sample work-up and analysis. The precision of the Soxhlet extraction and Kuderna-Danish concentration steps will be measured. The acid/base extractions for aqueous sample fractions from the Semi-VOST method will be studied for recovery of polar compounds. A series of experiments will also be conducted to investigate pyridine and other amine compound stability in methylene chloride.

References

1. U.S. Environmental Protection Agency. Test methods for evaluating solid waste: physical/chemical methods. EPA Report No. SW-846, U.S. Environmental Protection Agency, Washington, DC: 1982.

2. J.C. Harris, D.J. Larsen, C.E. Rechsteiner, and K.E. Thrun, "Sampling and Analysis Methods for Hazardous Waste Combustion." EPA Report No. 600/8-84-002, U.S. Environmental Protection Agency, Washington, DC: 1984.

3. U.S. Government Printing Office, Federal Register, 49(191), October 1, 1984, p. 38791.

4. R.M. Martin, Construction Details of Isokinetic Source Sampling Equipment. Report No. PB-203-60/BE, APTD-0581. U.S. Environmental Protection Agency, Research Triangle Park, NC: 1971.

5. U.S. Government Printing Office, Federal Register, 49(209), October 26, 1984, 40 CFR Part 136, pp. 153-174.

6. U.S. Environmental Protection Agency. Contract No. 68-02-3148, Work Assignment No. 6 - "Validation of the Semi-Volatile Organic Sampling Train and Associated Analytical Processes for Measuring Emissions from Hazardous Waste Incinerators," in progress.

7. J.A. Glaser, D.L. Forest, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Env. Sci. Tech., 15(12), December, 1981, pp. 1426-1435.

8. C.E. Rostad, W.E. Pereira, and S.M. Ratcliff, "Bonded-Phase Extraction Column Isolation of Organic Compounds in Groundwater at a Hazardous Waste Site." Anal. Chem., 56(14), 1984, pp. 2856-2860.